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THISD ALL-UNION CONFERENCE ON KLECTROCHEMISTRY, MOSCOW, DECEMBER 1950

K. M. Gorbunova, Moscow

The third All-Union Conference on Electrochemistry was held at the Department of Chemical Sciences, Academy of Sciences USSR, with the participation of representatives of scientific and industrial organizations. The great variety of subjects and methods, as well as ability to apply in practice the results of theoretical investigations, which is characteristic of USSR science, were apparent in the papers presented at this meeting. The type of work done in this field, enables one to understand that the most powerful electrochemical industry of the Soviet Union was created almost entirely on the basis of work accomplished by its own scientists and engineers.

In the main, the activities of the meeting were concentrated in the following fields:

- 1. Mechanism of electrode processes in solutions of electrolytes
- Problems of the theory and practice of electrodeposition of metals
- Problem of chemical sources of current
- Problems of electrolysis in the chemical industry

In opening the meeting, M. M. Dubinin, secretary of the Department of Laguer ical Sciences, Academy of Sciences USSR, emphasized that USSR electrochemists are faced with new and important tasks in connection with the Communist construction projects.

A report by M. A. Izgaryshev dealt with the history of national electrochemistry. In discussing developments that took place in the Soviet period, Izgaryshev mentioned V. A. Kistyskovskiy's investigations on phenomena of elec-trode passivity and on the electrochemical theory of corrosion as well as him own work on the hydrate theory of the origination of electromotive forces. He paid particular attention to electrochemical investigations dealing with processes of electrolysis that are important from the practical viewpoint, namely

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deposition and solution of metals, electrical oxidation and reduction, etc. (work done by himself, P. 3. Titov, N. T. Kudryavtsev, V. I. Layner, S. V. Gorbachev, O. A. Esin, I. G. Shcherbakov, etc.); noted the leading role played by USGR science in work on the theory of electrolytic deposition of metals (work by members of V. A. Kistyakovskiy's school; K. M. Gorbunova, P. D. Dankov, A. G. Samartsev, A. T. Vagramyan, etc.); mentioned investigations by N. I. Kobozov's group on the theory of hydrogen evervoltage; indicated that work on the electrochemical theory of correction carried out by V. A. Kistyakovskiy, himself, and G. V. Akimov was of importance for practical steps in combating corrosion; and stated that the outstanding work by A. A. Yakovkin, P. P. Fedot'yev, and a

In his report on the kinetics of electrode processes and phenomena at the boundary metal-solution, A. H. Frunkin mentioned work on the ctructure of the metal-solution boundary carried out by the Physicochemical Institute imeni L. Ya. Karpov, the Moscow State University imeni M. V. Lomonosov, and WFAN SSSR (Ural Affiliate, Academy of Sciences USSR) and stated that in the work in question, methods were applied and perfected which involved determinations of capacity, charging curves, wettability, adsorption, electrocapillary curver, etc. He furthermore stated that USSR electrochemists have also brought to a higher degree of precision methods for investigating electrochemical processes and cited as examples B. V. Breshler's use of alternating currents of various frequencies, V. A. Pleskov's application of isotope tracer atoms for characterizing exchange currents, V. G. Levich's work on the diffusion of reacting particles to the electrode surface, as well as the work of his own group (B. N. Kabanov, V. S. Bagotskiy, et al.) on the mechanism of processes occurring at high current densities and the effect of acidity on overvoltage.

great number of their collaborators and pupils was of special significance in the development of the USSR industry of light metals.

Frunkin discussed the nature of slow stages in the process of hydrogen discharge at electrodes with high or low overvoltage. He mentioned in this connection work on the discharge phenomenon itself, done by M. I. Kobozev and N. I. Kekrasov, who indicated the role of the energy of adsorption of atoms in determining the magnitude of the overvoltage; referred to the work of W. A. Izgaryshev, which brings out the importance of the solvation factor; and mentioned work by O. A. Yesin, N. D. Sokolov, and M. I. Temkin. He further mentioned investigations on the electrolytic separation and reduction of oxygen that were carried out by N. D. Tomashov, Z. A. Iofa, V. I. Veselovskiy, and others, and subjected to criticism the work of H. Eyring, Firthing, and Solt.

Frumkin then dwelt on work with the mercury dropping electrode which is ing conducted by his pupils. An important result of this work, according to him, is an explanation of the reasons for divergence between values obtained with a mercury dropping electrode and with a stationary electrode. This explanation was arrived at by considering hydrodynamic conditions that exist at a charged liquid surface.

Referring to work on the subject done by M. A. Loshkarev, T. A. Kryukova, et al., Frumkin mentioned in his report that the question regarding the mechanism of the effect of organic additives on the electrode process was first raised in the USSR by N. A. Izgaryshev. He further stated that he regards as an important achievement the finding to the effect that the potential of the zero point represents a value dependent on the nature of the metal, and that this value is connected with the work done by the electron leaving the metal (cf. S. V. Karpachev, et al.). Touching on the electrochemistry of nonaqueous solutions, Frumkin stated that the USST has occupied a leading position in this particular field ever since the work done by I. A. Kablukov; that N. A. Izgaryshev's first investigations were done in this field, and extensive research on the subject was conducted at the Ukrainian Academy of Sciences by V. A. Plotnikov, V. A. Izbekov, and others.

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Frunkin then briefly discussed the work on the electrolytic deposition of metals done by N. A. Izgarychev, K. M. Gorbunova, A. T. Vagramyan, A. G. Samaribachev and went into greater detail in reviewing investigations in the field of kinetics of electrode processes, which are closely connected with the very impuritions of Academician V. A. Kistyakovskiy and his school to this field, consisting, among other things, in the formulation of a film theory of passivity phenomena; and dwelt on the work by G. V. Akimov and collaborators on passivity problem.

Referring to the work of B. V. Ershler, B. N. Kabanova, and R. Kh. Eurshteyn, Frunkin pointed out that although typical phenomena of passivation and activation by ions can already be observed with a very low degree of filling of the surface, i.e., a degree of filling that is insufficient to form a monoatomic layer, the presence of somewhat thicker layers of oxides and salts must also be taken into consideration from this standpoint.

In characterizing the corrosion behavior of metals, Frumkin started from an assumption that all processes which take place simultaneously at the surface of the metal (the electrode) are statistically independent, and that their velocity is determined by the total value of the potential and diffusion conditions. He further stated that under the circumstances, the cathodic and anodic processes may take place in the same area of the surface if the surface is completely homogenous, while in cases of physically and chemically nonhomogenous surfaces, the velocities of these two processes will be different at any one pince, so that the areas at which cathodic or anodic processes occur on the surface will be separated from each other.

Thus, the type of corrosion damage to which various metals and alloys are exposed depends on the distribution of cathodic anodic zones, the nature of which has been subjected to thorough study on the basis of the theory of local elements advanced by G. V. Akimov, H. D. Temashov, et al. In conclusion, Frumkin stated that practical application of the theory of electrode processes to industrial end economic problems is still inadequate at this stage: there must be wider use of the theory for solving problems of the electrochemical industry, electrodeposition of metals, perfection of chemical sources of electrical power, and protection from corrosion.

During the following seven plenary sessions of the meeting, papers were presented on various theoretical problems and on methods for the investigation of electrochemical processes. Thus, during the second session, work on the mechanism of processes which cause overvoltage at electrodes during the separation of hydrogen, reduction of oxygen, etc., was discussed. In a report containing data on the mechanism of the reduction of oxygen and presented by V. S. Bagotskiy, who used a mercury electrode, and another report by A. I. Krasil' shchikev, who used solid electrodes, the conclusion was drawn that the addition of an electron to the oxygen molecule is the stage which determines the rate of the process. P. P. Turov read a paper in which he concluded on the basis of data on the decomposition potentials of acidic, neutral, and alkaline aqueous solutions, as well as of solutions in acetone, that the potentials of separation of hydrogen from acidic solutions and of hydroxyl ions from alkaline solutions are distinct from those required for the direct decomposition of water. He ascribed the appearance of "second potentials" to the decomposition of the solvent rather than the discharge of complex ions, as had been assumed by O. K.

The third session was devoted to problems either directly or indirectly connected with the corrosion of metals. The meeting decided to send greetings to V. A. Kistyakovskiy, who was a pioneer in this field in the USSR.

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polarization so that the rate of corrosion is small.

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In a paper by G. V. Akinov, a classification of types of corrosion damage was given. It was shown on examples that both in oxidizing and nonoxidizing medic, cases of a complete absence of the effect of admixtures, as well as cases of a teak or very strong effect, are observed. Akimov assumed a separation in space of zones in which clementary cathodic and anodic corrosion precesses take place and emphasized that this separation bears a dynamic character. Akimov showed that on the basis of data obtained with the aid of corrosion pobarization diagrams, the diverse effects of admixtures and inhomogeneities of structure on the rate of corrosion become understandable. Even when the initial difference of potentials is small (i.e., the metal is pure), there may still be considerable corrosion because of the absence of polarization; on the other hand, in the presence of admixtures which bring about inhomogeneities of structure, a great initial difference of potentials may be accompanied by strong

Yu. V. Baymakov and M. I. Zamotorine expressed the assumption in a paper presented by them that changes in the properties of electrolytic iron which occur on heating of hydrogen-containing deposits are caused by the transformation of a solid solution of protons in iron, which is stable at ordinary temperatures, into an atomic solution that is subject to subsequent decomposition. In another paper, G. S. Vozdvizhenskiy, V. A. Valeyev, and V. A. Dnitriyev advanced the concept of the decisive influence of texture on the process of anodic solution or oxidation of metals. In a report by B. N. Kabanov, it was shown that passivity of metals toward solutions may, in some cases, result from the presence on the surface of layers of oxygen which approach the lowest limit as far as thickness is concerned (these very thin layers occur on Fe, Al, and Mg), while in other cases, a thicker insulating layer is present.

In the discussion which followed, A. N. Frumkin desended the view that separation of anodic and cathodic areas in space during the process of solution of metals does not necessarily follow from the electrochemical nature of the process of solution. According to L. I. Antropov, this separation must occur in any electrochemical process.

In the fourth session, five papers were presented which discussed the mature of elementary electrochemical processes and the theory of concentration polarization. In V. A. Pleskov's paper, entitled "Investigation of the Ion Exchange Reaction Between the Electrode and the Solution by the Method of Radio-active Tracers," the possibility of using this method for investigating the state of ions that determine the potential and are in solution (i.e., the presence of complexes, their nature, etc.), as well as for the investigation of adsorption films which form on the electrode and strongly impede the ion exchange,

In a paper, "Energy of Activation and the Pre-exponential Factor in Electrochemical Processes," M. I. Temkin distinguished between the ideal and actual energies of activation and the corresponding pre-exponential factors. He also indicated methods for determining the actual energies of activation in such a manner that knowledge of the heat effect corresponding to the individual electrode process is not necessary, and for finding the pre-exponential factors corresponding to these energies. G. P. Faerman and Ye. D. Voeykov, in a paper read by them, expressed the opinion that metals and electron-conducting salts like AgS, CuS, HgS, and CdS are capable of exerting a catalytic effect on any oxidation-reduction reaction. In a report by V. G. Levich, data on convective diffusion and concentration polarization caused by it were presented.

In a discussion of the last group of papers mentioned, S. V. Gorbachev observed that in his own work, as well as that of N. P. Zhuk, A. V. Izmaylov, N. Ye. Khomutov, et al., an attempt has been made to bring the theory of electrolysis

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closer to ideas derived from chemical kinetics. However, according to Gorbachev, this problem cannot be formulated in a simplified manner, as has been done in M. I. Temkin's paper, where equations based on the theory of absolute reaction rates were mechanically applied to electrolytic processes. Within the temperature range up to 100°C, these equations show deviations from the Arrhenius equation by values which cannot be confirmed by any experimental data. The proportionality of the rate of reaction to the concentration, which is implied in these equations, as also contradicted by experimental data, while the linear dependence between the energy of activation and the potential cannot be confirmed either. In his reply to this, M. I. Temkin stated that when he calculated the rate of electrochemical processes, his task consisted precisely of the consideration of their specific characteristics. In the case of the discharge of hydrogen ions considered by him, proportionality between the reaction rate and the concentration has been proven experimentally; he assumes that this proportionality must also apply in other cases.

A. N. Frunkin called attention to an interesting discrepancy between V. A. Pleskov's data and the assumption made in the literature to the effect that during separation of a metal at a mercury electrode, the overvoltage is lower than in separation at a crystalline electrode. In Frunkin's opinion, the reason for the reverse relationship may be due to the gain of energy resulting from the formation of a crystal lattice.

At the fifth plenary session, papers dealing with general problems pertaining to the electrodeposition of metals were presented. K. M. Gorbunova and P. D. Dankov outlined the present state of the theory of crystallization and gave a classification of types of electrolytic deposits (from powders to dense coatings), based on the lew of distribution of active growth points over the surface of the electrode and taking into consideration the nature of the metal, of the ions in the electrolyte, and of the passivating effect of the solution. N. N. Balachova and A. T. Vagramyan discussed the mechanism of the deposition of metal from cyanide solutions and brought out that study of passivation curves led them to the conclusion that the electrode does not become passive in cyanide solutions.

S. V. Gorbachev showed that the work done by him and his group on the influence exerted by the temperature on electrolysis furnishes a very effective method for the investigation of electrolytic processes. A study of the effect of temperature permits differentiation between concentration, chemical, and "phase" polarization. The particular mechanism of polarization that prevails is determined not only by the nature of the electrode reaction but also by the concentration of the components of the solution and the magnitude of the polarization. In Gorbachev's opinion, an increase in the amount of polarization brings about a smooth transition from chemical to concentration polarization. The energy of activation then drops smoothly (but not according to a linear relationship) with the growth of the potential, gradually approaching the effective energy of activation /corresponding to?/ viscous flow of the solution. Gorbachev then pointed out that he and Ye. P. Starostenko discovered a new type of polarization, manual phase polarization.

Gorbachev further stated in his report that Volmer's theory of delayed discharge represented a very useful approach 20 years ago. However, at present, the followers of Volmer are vainly trying to fit the whole of electrochemistry into the framework of this theory, while experimental data in many branches of this science pass beyond the limits of the concepts formulated by the theory in question. Thus, according to Gorbachev, Volmen's theory characterizes incorrectly the effect of the electrolyte concentration; only rarely gives an accurate description of the dependence of current density on the potential; incorrectly expresses the effect of the temperature; and does not predict the existence of phase polarization. Gorbachev then suggested that the formal theory of delayed discharge, which unjustifiably claims universal validity, should be

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replaced by the more profound ideas of H. A. Izgaryshev's theory and the theories of H. I. Kebozev, A. G. Samartsev, K. M. Gorbunova, A. T. Vagranyun, L. I. Antropov, G. S. Vezdvizhenskiy, G. A. Akinov, H. D. Tomashov, H. T. Kudryavtsev, and other electrochemists, which are based on new investigations and discoveries.

In N. T. Kudryavtsev's paper, "Reasons for the Formation of Spongy Deposits on the Cathode and Mechanism of the Action of Added Tin and Mercury in Eincate Electrolytes," the author developed, on the basis of experimental data, the idea that a sporge forms because colloidal particles of gine which apparently have been detached from the anode in the process of its solution get to the anode. The added tin and mercury salts which suppress sponge formation bring about oxidation of the zine particles. These particles then go into solution. According to a paper presented by A. L. Rotiuyan, experimental data on the effects of the concentration of MisOh, MagSOh, Ma Cl, PM, and the temperature of the solution are in accordance with the equation based on A. H. Frunkin's theory of delayed discharge; an unusual dependence of the potential on the PM (exhibiting a maximum) that was discovered by him was treated in the light of N. A. Izgaryshev's mechanism of the action of colloidal additives (in this case, nickel hydroxide) on the magnitude of the cathodic potential.

The last paper at this session was read by N. Ye. Khamatov. On the basis of an analysis of experimental data on hydrogen overvoltage, this investigator came to the conclusion that there is a thoroughgoing interdependence between phenomena of hydrogen overvoltage, the structure of the electrode material, and the structure of water molecules and hydroxonium ions. A definite dependence between interatomic distances in metals and the values of hydrogen overvoltage, as well as oxygen overvoltage, was established. In Khomutov's opinion, an explanation of this dependence can be obtained in the light of N. A. Izgaryshev's and N. I. Kobozev's theoretical views on the nature of overvoltage, as well as by considering the geometric and energetic peculiarities of the transition state involved in the electrolytic separation of hydrogen.

A considerable portion of Khomntov's paper was devoted to criticism of the theory of delayed discharge. In Khomutov's opinion, this theory is essentially based on the physically unclear idea that a delay takes place in the fundamental process of neutralization of a proton with an electron. From this assumption, an equation results which cannot be confirmed in an unequivocal manner by experiment. The effect of p_Π on the overvoltage, which is predicted by the theory, cannot be verified experimentally in a number of cases.

During the discussion that followed, the following subjects were dealt with: problems connected with the electrolytic deposition of metals (P. D. Denkov), mechanism of the formation of spongy deposits (Yu. V. Baymakov), the problem of the inadequacy of existing methods for measuring overvoltage (A. T. Vagramyan), etc. The discussion on the reports presented by S. V. Gorbachev and H. Ye. Khomutov proceeded in a very sharp form. The critical statements made by them were objected to on the ground that they had underestimated the role of the work done by A. H. Frunkin and his pupils in developing the theory of electrode processes and of the significance of the theory of delayed discharge. The objections in question were made by M. I. Temkin, V. G. Levich, V. A. Pleskov, V. L. Kheyfets, V. S. Bagotskiy, B. N. Kabanov, A. I. Krasil'shchikov, and A. K. Lorents.

In the following session, papers dealing with the effect of surface-active agents on the course of electrochemical reactions were presented. This included reports by T. A. Kryukova, V. I. Melik-Gaykaayan, and A. P. Martirosyan on processes at the mercury electrode; by A. I. Levin on the deposition of copper on solid electrodes; and by Z. A. Iofa on processes of solution and etching of metals. In the work reported by Kryukova it was shown that inhibition of the

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electrochemical reaction coss not take place over the whole range of potentials in which an adsorption layer is formed on the surface of the mercury; this inhibition occurs within a more narrow range. In the authors' opinion, a definite structure of the adsorption layer must apparently be present. According to Levin, inhibition of the reaction is caused by presence at the electrode of a rigidly oriented diffuse polylsyer. Icfa discussed the action of inhibitors on the process of solution of iron in acids from the standpoint of selective adsorption of nolecules. At active points of the iron, this adsorption, according to him, has a greater effect on the anodic polarization of the metal than on the cathodic discharge of hydrogen ions.

In discussing the preceding reports, A. H. Frunkin stated that there are two kinds of adsorption layers. In some cases, the adsorption layer completely screens the surface, inhibiting the discharge reaction; in other cases, the reaction does take place in the adsorption layer itself, but is subjected to a certain amount of inhibition. In Frunkin's opinion, inhibition by the gel-like layer described in Levin's paper is doubtful; the reason for polarization must be interaction in a monomolecular layer.

The following group of reports which dealt with problems of electrochemical oxidation and reduction under participation of inorganic as well as evganic compounds was received with a considerable amount of interest. Daxing recent years, interest in this particular field of electrochemistry, which is capable of extensive development, has risen considerably.

H. A. Izgaryshev in a paper entitled, "Theory of Processes of Electroreduction and Electro-oxidation," pointed out that earlier ideas regarding the participation of atomic hydrogen or oxygen in processes of this type have been abandoned and replaced with the concept of direct discharging or recharging of polar groups adsorbed at the electrode. He mentioned in this connection that extraneous ions, which, from a purely formal standpoint, do not participate in the process of electrolysis, exert a substantial influence on its course. This influence apparently depends on the charge and radius of the ions. Izgaryshev also ascribed some importance to the capacity of extraneous ions to dehydrate ions which actually take part in the process.

The mechanism of electrolytic oxidation was discussed in the following reports: S. V. Gorbachev's and N. P. Zhuk's on the anodic oxidation of chlorine, T. S. Filippov's on the formation of chlorates, and D. P. Semchenko's and G. K. Il'in's on the oxidation of chlorine amions in hydrochloric acid into amions of chloric acid.

A paper by H. Ye. Khomutov and S. V. Gorbachev on the electrolytic oxidation of aniline aroused a lot of interest. On the basis of an extensive study of the process, the authors of this paper arrived at the conclusion that an autocatalytic electrode reaction proceeding according to a polymerization scheme takes place. The velocity of this reaction is determined by the stage in which protons are split off from the molecules being oxidized.

Papers on the mechanism of electrolytic reduction were presented by A. I. Shlygin and M. B. Neyman. Shlygin's paper dealt with the reduction of unsaturated organic substances on platimum, and Neyman's, with the reduction of unsaturated aldehydes and actions at a dropping mercury cathode. During the discussion, particular attention was paid to two problems: that of obtaining kinetic data for processes which take place at metal anodes and that of the role played by extraneous ions in processes of electrolytic oxidation and reduction. T. S. Filippov, Gorbachev, and A. H. Frumkin remarked that evolution of oxygen at an electrode brings about irreversible changes in the surface of the electrode. The resulting indefinite state of the surface of the electrode is the

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reason why reliable kinetic data on processes that are accompanied by the evolution of oxygen is not yet available, although many investigations on the subject have been carried out.

L. I. Antropov pointed out that A. I. Shlygin's work leads to the conclusion that the recombination mechanism of hydrogen overvoltage on platinum plays a considerable role in the phenomenon involved and indicates that the oun total of experimental data for a platinum cathode cannot be interpreted from the standpoint of the theory of delayed discharge. Antropov further stated that Shlygin, in his treatment of the hydrogenation of organic compounds, did not take into consideration the value of the potential corresponding to a zero charge of the metal.

During one of the last sessions of the meeting, a number of reports dealing with the theory of the electrode potential and problems connected with the points of zero charge of metals was presented. In a paper read at this secsion, B. V. Ershler indicated that the problem of the absolute potential, i.e., of the potential jump at the boundary metal-solution, has lost its importance. At the same time, he stated that difficulties connected with establishing the distribution of charges on the interphase boundary interfere with the calculation of the absolute potential. Ye. A. Kanevskiy defined the absolute potential differently in his report (not as the potential jump mentioned above). Establishing the described the possibility of determining it by means of a thermodynemic calculation starting from data on the actual energy of hydration and cited a table of values for absolute potentials.

Of considerable interest was L. I. Antropov's report, in which the author summarized published data on points of zero charge and graphically correlated it with the working-state intervals [literally, "intervals of working regimes"] for various electrochemical processes in which the metal in question participates. This includes discharge at the metal of hydrogen, electrolytic reduction of organic compounds, electrodeposition of the metal involved, and corresion of this metal. By reason of the fact that adsorption of various surfaceactive substances on a metal exerts a significant effect in the potential range adjacent to the point of its zero charge, the possibility of evaluating the effect of surface-active additives and of using the right additive for the desired modification of the process exists. An experimental check carried out by Antropov confirmed that not only the rate but also the direction of the electrode process depends on the location of the point of zero charge.

In a paper presented by Ya. M. Kolotyrkin, an analysis was made of the effect which the point of zero charge has on processes that determine hydrogen overvoltage on lead, cadmium, and thallium. The method used by this investigator permitted him to demonstrate that modification of the overvoltage in different regions of polarization is described by two curves of the same Tafel tyre but having different coefficients. Supplementary experimental material, particularly on the effect of cations and surface-active anions on the overvoltage at different polarizations, indicated that transition from one type of the curve to another takes place in the vicinity of the point of zero charge of the metal surface.

A report by T. I. Borisova cited data characterizing the state of anodicelly polarized surfaces of Ag, Ni, and Fe in alkaline solutions and of Pt in acidic solutions, which were obtained by the method of separate determination of the capacity and ohmic resistance components of an electrode during passage of an alternating current. In addition to this, Borisova presented new data on the zero charge points of silver and platinum.

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During the discussion of the preceding papers, in which many electrochemists participated, one of the participants, P. V. Galushko, pointed out that the problem of the absolute potential is of a philosophical nature. Ke suggested that valuable material contained in the writings of F. Engels be utilized in work on this problem.

A lively discussion of the reports presented at sectional meetings took place. There were altogether three sessions of the section of electro-deposition two sessions of the section of chemical sources of current, and one session of the section of technical electrolysis. Problems pertaining to practical electroplating and electromatallurgy were dealt with 10 four of five reports. Among them, one should note particularly the reports of P. S. Titov and H. D. Lyozner, who investigated the conditions for rapid isolation of copper from cyanide solutions; A. I. Levin's paper on the conversion of copper ancdes that contain nickel; and P. P. Belynev's paper on lead plating in alkaline solutions.

Just as at the preceding conference on electrochemistry (Kiev, 1949), the problem of the effect exerted on the surface of an electrode on adhesion and uniformity of the deposit elicited considerable interest. This problem was touched on in papers presented by L. I. Kadaner and P. P. Belyayav. New data on the structure of the surface of ordinary and brilliant nickel, which was obtained for the first time with the aid of an electron microscope, and general considerations in regard to conditions under which brilliant surfaces are formed on electrodes were presented in a paper written by K. M. Gorounova, T. V. Ivanovskaya, and S. S. Popova. Only one report, that of K. P. Batashev, was concerned with problems of electrolytic polishing. In G. V. Forsolom's paper, the influence of work done by V. P. Masovets and his group on calculating the field distribution in electrolytic cells was perceptible. Extensive material obtained as a result of ultramicroscopic investigations and characterizing conditions under which colloidal particles form and migrate at the cathode was presented in a report given by M. N. Polukarov.

It is to be regretted that no reports on new types of protective coatings and alloys were presented at the sectional meetings.

As far as activities of the section of chemical sources of current are concerned, four reports of the ten that were presented dealt with processes at electrodes and effects of conditions at the electrodes and of additives on the operation of lead storage batteries. A report by A. S. Kolosov discussed the role of iron in the operation of cadmium-nickel storage batteries. Three reports were devoted to processes taking place at the oxide electrodes of galvanic elements: a report by P. D. Lukovtsev and S. A. Temerin, which discussed the nature of processes taking place at actual oxide electrodes; a report by S. A. Gantman and P. D. Lukovtsev, in which various aspects of oxygen overvoltage at an oxide-nickel electrode were discussed; and a report by V. S. Daniel'-Bek on the theory of metal-oxide-graphite electrodes.

The reports and discussions in the section of technical electrolysis demonstrated extensive possibilities of utilizing more widely experimental results and methods of electrochemical kinetics for the solution of applied problems of the basic chemical industry.

In the final plenary session, discussions on the reports made by W. A. Iz-garyshev and A. N. Frumkin took place. In this discussion, which attracted considerable attention on the part of a large audience that was present, problems raised in other reports were also considered. The time was somewhat inadequate, so that complete agreement could not be achieved between various divergent directions in theoretical and experimental research.

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- 3. V. Gorbachev, in his talk, expressed dissatisfaction with A. H. Frunkin's rep(rt, in which, according to him, the achievements of other schools of electrochemistry were not adequately reflected. He further pointed out the limited range of problems on which Frunkin's school works and its lack of a tendency to apply results in practice. Gorbachev then subjected to criticism the excessive expansion of work on the theory of delayed discharge, to which, according to him, numbers of Frunkin's school attach undue importance, while they neglect work on other, more essentia) problems.
- G. V. Akimov concentrated on raising objections to Frunkin's idea that cathodic and anodic processes can take place in the same region of the metal surface. Akinov advanced a number of arguments based on structural characteristics of the surface and body of metals in an attempt to show that this idea is wrong; he also pointed out that one cannot speak of an electric current when a difference of potentials is absent. At the same time, Akimov remarked that cathodic and anodic regions may interchange places during the process of corrosion. In conclusion, he pointed out that Frunkin did not cite a number of achievements by USSR corrosion specialists, although these specialists have created a large specialized field of electrochemistry which is necessary for the understanding of corrosion. Among the achievements of USSR corrosion specialists; Akimov listed the theory of irreversible electrode potentials, the theory of processes taking place under oxygen depolarization, the theory of electrochemical processes proceeding in the galvanic microelements of the system, the theory of multielectrode systems, and finally, the method of polarization diagrams. In concluding his talk, Akimov stated that one must reconsider the positions from which further development of electrochemistry is to take place to make sure that young technical men will be educated in the spirit of new and fresh ideas.
- V. P. Lebedev and V. G. Sindyukov also criticized the results which Frunkin's school obtained by developing further the theory of delayed discharge. They stated that the theory of delayed discharge, which was borrowed from foreign scientists and supplemented by Frumkin and his collaborators, is incapable of explaining the majority of electrochemical processes.
- V. A. Pleskov, M. A. Loshkarev, and M. I. Temkin took issue with this evaluation of the originality and applicability of the theory of delayed discharge Pleskov stated that this theory should not be set apart from other theories: it can be confirmed by experimental data in many cases, as it has been in the perticular case of the report given by Ya. M. Kolotyrkin at this meeting. At the same time, Pleskov recognized as justified the objection that the theory of delayed discharge has not yielded adequate practical results. Loshkarev suid that the direction in which the work of Frumkin's school is pursued, represents one of the original developments of USSR electrochemistry.
- V. P. Galushko, in his talk, dwelt on the necessity of using the work of Marxist classics to solve many of the problems discussed at the meeting, such as the problem of the source of energy and localization of potential jumps in galvanic elements; an analysis from the standpoint of dialectical materialism would prevent idealistic misinterpretations of the nature of the problem there.
- I. I. Koval' said that practical activities should be brought into closer contact with the work of scientific research institutions.
- M. S. Fortunatov expressed doubts in the correctness of V. A. Pleskov's assertion to the effect that Tafel's equation is valid in a wide range of current densities. He gave an original interpretation to Ya. M. Kolotyrkin's results, which cover the potential ranges on both sides of the zero charge; according to Fortunatov's conclusion, the plotting of these results in the potential-current coordinate system yields a typical curve showing a second potential, which was described by O. K. Kudra and received with strong reservations by a number of electrochemists.



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A number of speakers (V. A. Zarinskiy, A. L. Rotinyan, and others) indicated the necessity of publishing, as soon as possible Soviet textbooks, and monographs.

A. H. Frumkin, in his concluding talk, reviewed the activity of his school in the light of the criticism leveled against it. He also indicated the errors committed by him in the capacity of leader of one of the directions of USSR electrochemistry. Frunkin, furthermore, discussed briefly the question of priority of the idea involved in the theory of delayed discharge and the role of solvation factors, a matter which became clear to him only recently. Incorrectly ascribed to M. Volmer, this idea was expressed considerably earlier by M. A. Izgaryshev. The idea in regard to the delay involved in solvation processes was originally formulated by the Kazan' professor, R. A. Kolli, in 1878. While now placing a high value on N. A. Izgaryshev's merits in the matter by recognizing that he emphasized the significance of solvation factors which determined a wholesome, progressive development in electrochemistry, Frunkin stressed that Volmer had made the first attempt to formulate quantitatively the concepts involved in the idea of delayed discharge and had demonstrated that an equation which agrees with Tafel's equation, based on experimental data, follows from them. Frunkin further noted that the ideas in regard to solvation were first formulated quantitatively in his, Frunkin's work. It was subsequently demonstrated experimentally that it is the transition of the ion into the adsorbed atom which is delayed: this is what determines the specificity of electrochemical kinetics.

On the basis of these facts, A. N. Frumkin stated that he regards as unjustified reproaches to the effect that the whole work of his school was concentrated on verifying one formula only, while all stages of the process not covered by this formula were neglected. Frumkin further rejected criticism to the effect that he did not give due credit to N. I. Kobozev. He then stated that he had never asserted that complete knowledge of any electrochemical process can be gained exclusively on the basis of the theory of delayed discharge; at the same time, he was unable to discern any new ideas in the work of S. V. Gorbachev which permitted clarification of interesting data on the electrolytic oxidation of aniline and the separation of chlorine (cf reports by Gorbachev's collaborators at the present meeting). In conclusion, Frumkin dwelt on errors committed by him which are subject to speedy correction, i.e., lack of attention to the history of national electrochemistry, as a result of which he failed to recognize the priority of Russian scientists in many fields, and insufficient attention to industrial applications.

The chairman of the last session, Ya. M. Kolotyrkin, summarized the work of the conference in a brief speech, pointing out that in the course of its work keen criticism of the substance of investigations carried out in the field of electrochemistry was applied for the first time so that faults which interfere with the development of USSR electrochemistry were disclosed. Kolotyrkin further expressed the hope that this criticism will be received in the right spirit and will form the basis for further constructive work by all active schools of electrochemistry.

The resolution passed by the conference considers it necessary to develop primarily activity along the following lines: (1) investigations dealing with the mechanism of the most important reactions of electro-oxidation and electro-reduction; (2) electrochemical production of a number of new, technically important metals; (3) work on lowering the expenditure of power and increasing the efficiency of industrial electrolysis; (4) creation of powerful chemical sources of current; (5) improvement of the quality of corrosion protection of metals; and (6) investigation of electrode processes in melts. It noted that the successes and shortcomings of USSR electrochemistry have been correctly reflected at the conference and that the basic directions to be taken by future research

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have been marked out. The resolution also noted that USEE electrochemistry has saids considerable progress as a result of work carried out by an extensive network of academic institutes, specialized branch institutes, and laboratories of higher educational institutions.

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